Table 1
The iodine content of samples of Barents Sea water

(The columns give the number of the station and its sonic depth in brackets, the sampling depth in m, temperature, chlorinity, and the iodine content in mg-at./m³.)

Station	Depth (m)	Temperature	Chlorinity	Iodine
1 (230)	0	6·15	19·12	0·46
–	181	4·40	19·16	0·52
5 (260)	0	4·30	19·31	0·54
–	241	–0·42	19·35	0·79
9 (350)	0	3·16	19·37	0·53
–	337	–0·72	19·36	0·57
14 (176)	0	4·27	19·43	0·51
–	154	1·22	19·41	0·50
18 (296)	0	6·21	19·35	0·83
–	276	3·87	19·43	0·91
20 (350)	0	6·91	19·16	0·50
–	300	3·24	19·31	0·51
22 (330)	0	7·89	19·04	0·50
–	193	5·71	19·36	0·51
26 (440)	0	7·13	19·41	0·50
–	389	3·00	19·40	0·55
28 (265)	0	3·38	19·30	0·52
–	244	0·86	19·36	0·67
29 (50)	0	2·29	19·18	0·49
33 (310)	0	4·57	19·18	0·52
–	272	2·27	19·41	0·53
38 (406)	0	0·41	17·86	0·50
–	100	3·93	19·44	0·53
–	200	2·77	19·38	0·58
–	400	2·32	19·38	0·50
45 (67)	0	–0·35	18·02	0·46
50 (440)	0	6·97	19·40	0·53
–	381	2·68	19·44	0·60
55 (280)	0	9·17	18·94	0·49
–	173	5·74	19·18	0·56

of analysis are employed, i. e., whether the differences found are caused by analytical errors, by regional and seasonal variations of iodine content, or by all these factors.

Experimental

Arsenic (III) salt solution. 1·98 g of arsenic trioxide (or an equivalent amount of sodium arsenite) is dissolved in 200 ml of water containing 1 ml of concentrated sulphuric acid. 50 g of sodium chloride is dissolved in another 200 ml of water. The clear solutions are mixed, 40 ml of concentrated sulphuric acid added, and the mixture diluted to 500 ml.

Cerium (IV) solution. 12·652 g of cerium ammonium sulphate $(Ce(SO_4)_2·2(NH_4)_2SO_4·2H_2O)$ is dissolved in water, 44 ml of concentrated sulphuric acid added, and the solution diluted to 1000 ml.

Water. All water used was redistilled from a solution containing about 2 g of NaOH per litre.

Procedure. 20 ml of sample (or suitable dilution) is transferred to a Beckman cell test tube (22 mm) and 2 ml of arsenic (III) salt solution is added.

The tubes are then placed in a thermostat so that the surface of the reagent mixture lies below the water level of the thermostat. After 20—30 minutes 2 ml of cerium (IV) solution is added to each tube of the series at intervals of one or two minutes and mixed well. During the last minute of the reaction time the test tube is transferred to the spectrophotometer (a Beckman model B was used in this work) and the extinction due to the cerium (IV) ions at a wave length of 4200 Å is read exactly after the chosen length of reaction time (counted from the moment the cerium (IV) solution was added) and again after intervals of one or two minutes.

Different calibration curves should be made for several temperatures and reaction times and when new reagents are introduced. Ten samples are prepared for this purpose from a standard potassium iodide solution containing 0·1 micrograms of iodine per millilitre. In each series of determinations the calibration curve is checked using at least three simultaneously treated standard samples.

The volume of the sample, the temperature, and the reaction time were chosen to make the differences in extinction as great as possible. At 25°C, for instance, 0·16 micrograms per 20 ml sample was the upper limit when the reaction time was 30 minutes. When the concentration of iodine exceeds this level a greater dilution or a shorter reaction time must be chosen. As in kinetic work in general, special care should be taken to keep each procedural detail constant.

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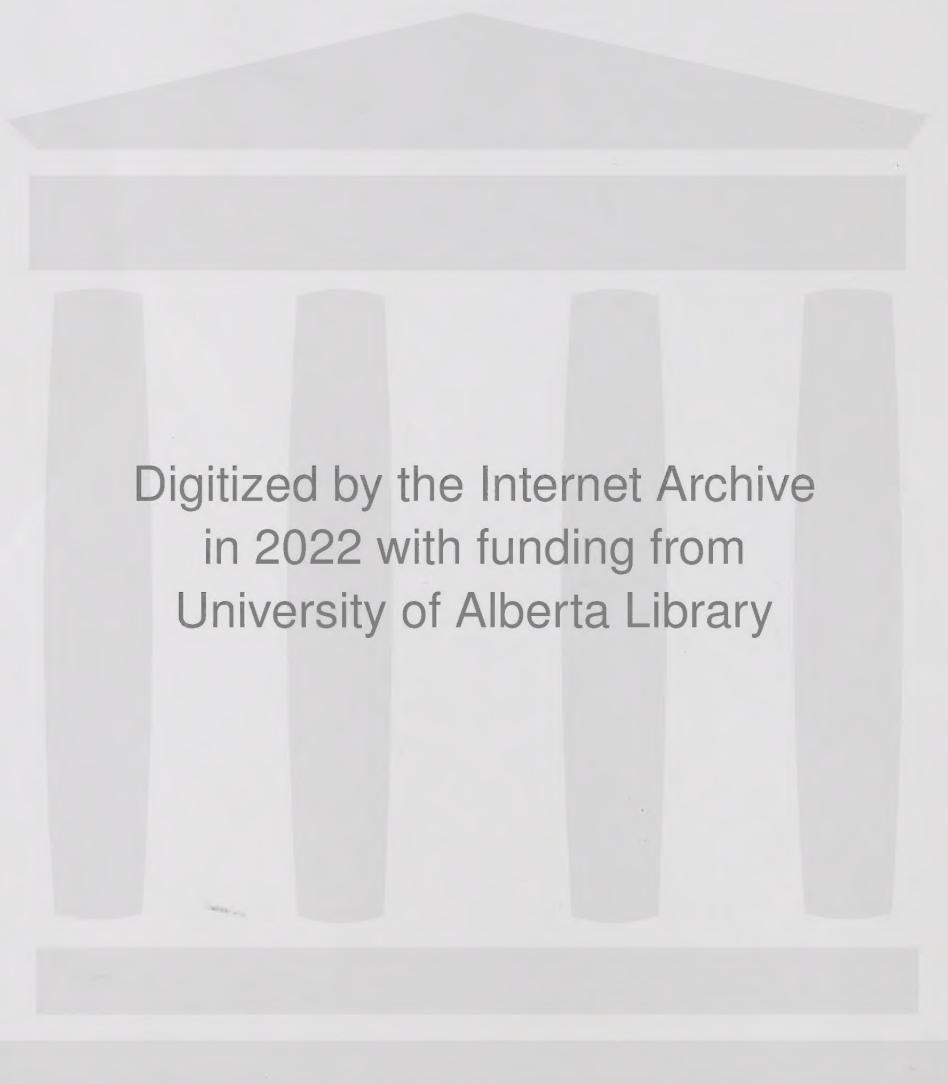
4.

The Iodine Content of Barents Sea Water

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The cycle of iodine in the hydrosphere and atmosphere forms one of the most interesting problems of geophysical chemistry. Divergent views on the form in which iodine occurs in sea water have been presented by several scientists in recent years (Shaw and Cooper, 1957 and 1958; Sugawara and Terada, 1958; Johannesson, 1958). Despite the known significance of this element relatively few data on the total iodine content of sea water have been reported. The greater part of this work has been done by Sugawara and Terada using an analytical method they have developed in which the halides are precipitated with silver nitrate, the iodide converted into iodate, cadmium iodide added to the silver iodate to yield an amount of free iodine six times greater than the amount in the original sample, and finally a spectrophotometric determination is made of the complex formed by the iodine with starch. By this method they have estimated the iodine content in sea water to be about 0·30 mg-at./m³. The previously accepted value was about 0·40 mg-at./m³ (Harvey, 1955). Recently a new method has been developed by Dubrowcic for the determination of iodine in natural waters (1955). This method is based on the catalytic effect of iodine on the redox reactions between cerium (IV) ion and arsenic (III) compounds. Chloride ions also catalyse the reactions but by adding a large amount of sodium chloride this effect can be kept constant. Furthermore, Dubrowcic found that in a medium of high chloride content the several forms of inorganic iodine exhibit similar catalytic activity. The catalytic method of iodine determination has also been used in clinical chemistry where it is widely applied in the determination of serum iodine; this provides a very good argument for the validity of the method. When planning the work described below the author found only one value for the iodine content of sea water as determined by this method. Dubrowcic reported that Adriatic Sea water contains 0·48 μg-at./1 of iodine. Therefore, in order to obtain additional data, the catalytic method was applied to the analysis of the iodine in 30 samples of sea water taken in the Barents Sea. However, in a paper presented at the First International Oceanographic Congress in New

York in September 1959, Barkley and Thompson (1959) reported some results of their analyses of iodine in sea water. For total inorganic iodine they found values varying between 0·30 and 0·60 mg-at./m³; the highest values were found for samples from North Pacific and Arctic stations.

The general sampling technique and the hydrographical data have been reported by Hela and Koroleff (1958). The approximate positions of sampling stations are shown on the chart (this volume, Fig. 1, p. 12). The water samples were collected in Pyrex glass vials which were sealed by fusion as soon as possible. The analytical method was in principle the same as that described by Dubrowcic, but, instead of stopping the reaction by adding ferrous sulphate, the extinction due to the cerium (IV) ions was measured spectrophotometrically at 4200 Å after a fixed period of time. The reaction mixtures were kept in Beckman test tubes in a thermostat for 29 minutes after the reagents had been added to the water samples and mixed: the tubes were transferred during one minute to the spectrophotometer and the extinctions read at exactly 30 minutes from the time of mixing. The fact that the reaction mixture was not in the thermostat during the short period required for the transfer and the measurement of the extinction could not cause any great error because the temperature coefficient of the reaction rate is rather low, the activation energy having the value 9·27 kcal/mole (Moran, 1952). On the basis of repeated measurements the experimental error is believed to be less than ± 5 per cent.

The results collected in Table 1 show the total content of inorganic iodine to be about 0·50 mg-at./m³ or more, but never much less. The mean value of all analyses is 0·56 mg-at./m³. Surface water contains as a rule less iodine than water from a greater depth; the mean value of the former samples is about 10 per cent lower than that of the latter samples. The iodine values will not be discussed in detail in this connexion as the main purpose of this paper is to draw attention to our poor knowledge of the total iodine content of sea water. Extensive studies are needed to determine why so different results are obtained when different methods